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STUDIES IN THE UREA SERIES. TRANSFORMATIONS OF  
NITROGUANIDINE.

BY TENNEY L. DAVIS AND ARMAND J. J. ABRAMS.

(Continued from page 3 of cover.)

## VOLUME 61.

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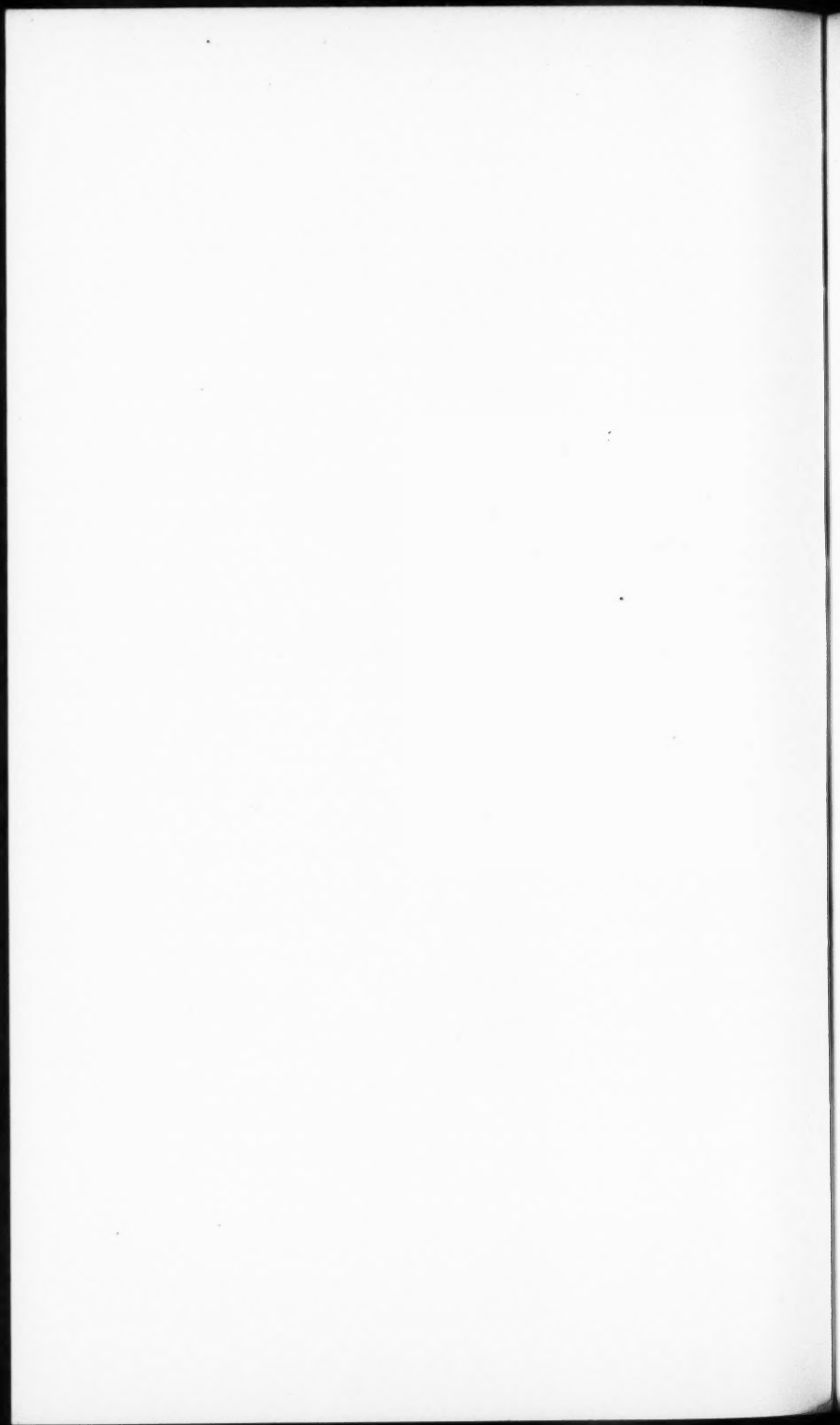
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Urea, thiourea, guanidine, and many of their derivatives, when heated, break down—often in more than one manner—to yield precisely those smaller molecules by the direct combination of which the urea derivatives may be synthesized.<sup>1</sup> Since the breaking down is orderly and predictable, it has been called the *urea dearrangement*, that name being chosen in preference to “disarrangement” which connotes a disorderly breaking down and in preference to “dissociation” or “disassociation” which names now commonly apply to the breaking apart of more or less polarized atoms or molecules. The urea dearrangement may be defined as the breaking down of a urea derivative in such manner that the hydrogen atom, previously attached to one of the nitrogen atoms, goes off in combination with the other nitrogen atom and the atoms or groups originally attached to it, deserting the rest of the molecule. It gives rise to ammonia or a substituted ammonia and to cyanic acid or a substituted cyanic acid. If each nitrogen atom of an unsymmetrical urea derivative carries an hydrogen atom, two modes of dearrangement are possible and occur simultaneously.

Many reactions then in the urea series consist in the direct combination or un-combination of electrically neutral molecules, without metathesis, in a predictable manner, thus—

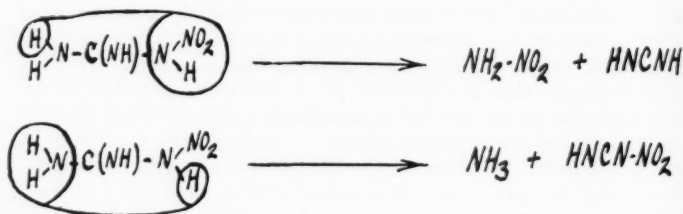


Referring to the diagram above, it may frequently happen that the substances, *A* and *B*, and consequently the urea derivative itself, are easily prepared and readily accessible. The substance, *C* or *D*, may be one which is much desired as a material for synthesis, but which

<sup>1</sup> *Jour. Amer. Chem. Soc.* 44, 2595 (1922); 45, 1816 (1923); *Proc. Nat. Acad. Sciences.* 11, 68 (1925).

cannot be obtained easily or is very expensive or difficult to handle. If, however, the urea derivative is heated with a substance with which *C* is capable of reacting, it dearranges reversibly to form *A*, *B*, *C*, and *D*; *C* is removed from the equilibrium, *A* and *B* recombine to form the urea derivative which produces more of *C*, and the urea derivative for the purpose of the synthesis acts as a convenient source of its dearrangement product. By working on this principle we have prepared from nitroguanidine certain substituted guanidines on the one hand, and substances of a new type, the alkyl nitroguanidines, on the other.

Nitroguanidine differs from urea in having a nitro group in place of an hydrogen atom and an imino group in place of the oxygen. It would be expected to dearrange in two modes, as follows—



The reactions of nitroguanidine when dissolved in conc. sulfuric acid suggest that dearrangement occurs in this solvent. Its reactions in water solution support the belief that in aqueous solution it dearranges in both modes. When it is decomposed by heat, cyanamide and ammonia are produced as such, and the other products are precisely those which would result from the decomposition, polymerization, and interaction of the expected dearrangement products.

The experiments which are described in the present paper, unless otherwise stated, were carried out with the more common and more stable *alpha* form of nitroguanidine.<sup>2</sup> Among the products of its decomposition by heat we have found a certain quantity of the unstable *beta*-nitroguanidine.

Nitroguanidine is a powerful explosive, remarkable for the fact that it is exceptionally cool. It has been used in mixture with colloided nitrocellulose for the manufacture of flashless propellant powders. These powders have the same ballistic power, weight for weight, as

<sup>2</sup> *Jour. Amer. Chem. Soc.* 47, 1063 (1925).

powders made entirely from nitrocellulose, but have the disadvantages that they produce a thin gray smoke and yield gases which contain ammonia. The presence of these products is readily explained by an understanding of the decomposition of nitroguanidine by heat.

#### REACTIONS OF NITROGUANIDINE IN CONC. SULFURIC ACID SOLUTION.

Nitroguanidine dissolves readily in cold conc. sulfuric acid and precipitates out again if the liquid is diluted with water. If its solution in this reagent is heated, nitrous oxide comes off, and ammonia and carbon dioxide are produced quantitatively in accordance with the equation,



but a long continued heating at an elevated temperature is necessary to complete the decomposition.<sup>3</sup> Indeed, the nitrous oxide comes off first and fairly rapidly, while the carbon dioxide comes off later and more slowly, a fact which suggests that the solution contains not one substance, the nitroguanidine, but two or more substances, the rearrangement products, one of which is attacked by warm sulfuric acid more readily to yield nitrous oxide, the other less readily to yield carbon dioxide. Moreover, the production of nitrous oxide is not quantitative: the gases contain elementary nitrogen as would be expected if nitroamide were present in the solution.<sup>4</sup>

Although a solution of nitroguanidine in conc. sulfuric acid appears to contain little or no nitric acid (for it yields nitrous oxide when heated), it nevertheless contains some substance which is capable of ready conversion into nitric acid, for it gives up its nitro group quantitatively in the nitrometer<sup>5</sup> and the solution has been found to be a satisfactory reagent for the nitration of such substances as aniline, phenol, and acet-*p*-toluide, which are soluble in conc. sulfuric acid. It seems unlikely that the nitric acid effective in these reactions is produced from guanidine nitrate resulting from the hydration of nitroguanidine, for in that case the nitric acid would be free in the strongly acid solution and would distil out when it is heated. If it is produced in the solution by the hydration of nitroamide or of nitro-cyanamide from the rearrangement, then cyanamide would be left in the solution after the nitric is removed. We have found that cy-

<sup>3</sup> *Jour. Amer. Chem. Soc.* 44, 868 (1922).

<sup>4</sup> *Jour. Amer. Chem. Soc.* 47, 1043 (1925).

<sup>5</sup> Cope and Barab, *Jour. Amer. Chem. Soc.* 38, 2552 (1916).

anamide in ammoniacal solution reacts slowly with ammonium picrate in the cold to produce guanidine picrate, and believe that we have found evidence of cyanamide in a sulfuric acid solution of nitroguanidine by treating the solution with an excess of aniline for the removal of nitric acid, diluting, making ammoniacal, adding ammonium picrate, and obtaining guanidine picrate.

#### REACTIONS OF NITROGUANIDINE IN AQUEOUS SOLUTION.

If nitroguanidine in aqueous solution dearranges reversibly to form on the one hand nitroamide and cyanamide, on the other ammonia and nitrocyanamide, the effect of adding ammonia to the liquid would be to disturb the equilibrium and to restore a part of the nitroguanidine which had broken down into ammonia and nitrocyanamide. The excess ammonia would also react with the cyanamide to produce guanidine. If the solution were warmed, the nitroamide would break down into water and nitrous oxide, the nitrocyanamide, by analogy with the known reaction of other nitroamines, would probably break down into nitrous oxide and cyanic acid, and the cyanic acid would combine with ammonia to form urea. All of these things appear to happen, for nitroguanidine on treatment with ammonia water yields guanidine and urea. The guanidine takes up carbon dioxide from the air and is obtained as carbonate.

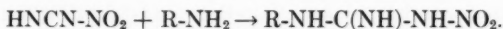
Guanidine carbonate may be obtained in a yield equal to about 40% of the theoretical amount by evaporating a solution of nitroguanidine in a large excess of strong ammonia water slowly on the steam bath, and results practically pure if the dry residue is washed with alcohol for the removal of urea. The same material is produced in a yield of about 90% when nitroguanidine is digested at 65° with an excess of ammonium carbonate in aqueous solution. Nitrous oxide comes off, and after 10 or 12 hours the nitroguanidine has disappeared entirely. The residue from the evaporation of the liquid consists of guanidine carbonate along with small amounts of urea and of melamine. The last-named substance supplies further probable evidence that cyanamide was present in the solution. The guanidine carbonate is entirely free from nitrate, and this method appears to be preferable, for the preparation of pure material, to the more usual double decomposition methods which involve repeated crystallizations.

When nitroguanidine is repeatedly recrystallized from the same water or refluxed for some time in water solution, the liquid becomes distinctly ammoniacal. The dearrangement products evidently react among themselves to produce guanidine, for ammonium picrate,

added to a solution which had been refluxed for 60 hours, yielded guanidine picrate equal to 1.6% of the total amount of possible guanidine.

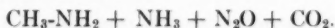
When nitroguanidine is heated with aqueous methylamine solution in a sealed tube at 100°, or boiled under reflux with the same reagent, a small amount of methylguanidine is produced. Refluxed with aniline in water solution it yields a very small amount of phenylguanidine along with phenylurea and a considerable amount of *sym*-diphenylurea. The substituted guanidines are evidently produced from cyanamide, the phenylurea from cyanic acid resulting from the decomposition of nitrocyanamide, and the diphenylurea as would be expected from the phenylurea in boiling aqueous solution.

More interesting results are obtained by working with aqueous solutions at temperatures (60°–70°) at which the nitrocyanamide would be expected not to decompose and accordingly to react with the amines to produce substituted nitroguanidines, thus—



When a suspension of nitroguanidine in water containing a molecular equivalent of methylamine is warmed to 60° or 70°, the nitroguanidine disappears rapidly, ammonia comes off in abundance, and the reaction is complete within a few minutes. The methylnitroguanidine is separated from unchanged nitroguanidine by solution in alcohol from which solvent it may be recrystallized. The residues contain methylguanidine. *Alpha*- and *beta*-nitroguanidine yield the same product.

Methylnitroguanidine dissolves readily in cold conc. sulfuric acid. If the solution is warmed, nitrous oxide comes off first, then a gas which extinguishes a glowing splint, and the remaining liquid, if diluted, made alkaline, and distilled, yields methylamine. The reaction indicates the structure which would be expected from the method of synthesis, namely, that in which the nitro group and the methyl group are attached to different nitrogen atoms, and is evidently as follows—



If the nitro group and the methyl group were attached to the same nitrogen atom, methylamine would probably not be produced, for methylnitramine is decomposed by strong sulfuric acid to produce

nitrous oxide which escapes and methyl alcohol which reacts further with the acid.<sup>6</sup>

We have prepared other substituted nitroguanidines from ethyl, *n*-butyl, and benzyl amines, but have been unable to prepare phenyl-nitroguanidine from aniline by the same reaction. In the preparation of benzyl-nitroguanidine, benzylurea was found in the reaction mixture, a fact which suggests that the nitrocyanamide in part combines with the benzylamine and in part breaks down to form cyanic acid which then combines with the base. The alkyl-nitroguanidines are soluble in water, in alcohol, and in conc. sulfuric acid, and give up their nitro group quantitatively in the nitrometer. They are being studied further in this laboratory. Benzyl-nitroguanidine is soluble in alcohol, but less soluble in water than nitroguanidine itself. It chars when treated with conc. sulfuric acid.

#### DECOMPOSITION OF NITROGUANIDINE BY HEAT.

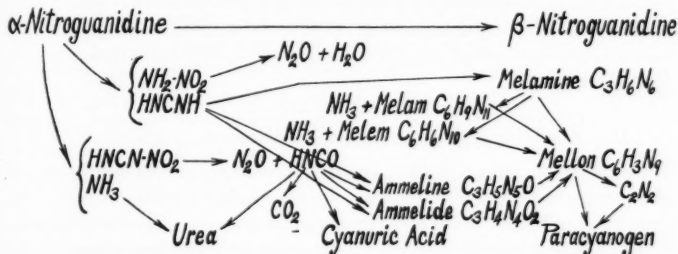
If a small quantity of nitroguanidine is warmed in a test tube, it melts at about 232° to a colorless liquid which effervesces, turns yellow and effervesces more violently, giving off water, and ammonia, and other material which collects as a white sublimate in the upper part of the tube, and leaves a buff colored residue which becomes bright yellow on stronger heating. If the tube, after cooling, is rinsed out with water, the wash waters show the presence of cyanamide when tested with copper sulfate or with ammoniacal silver nitrate. In some experiments the wash waters showed the presence of cyanic acid by Werner's test,<sup>7</sup> in others they failed to do so. Working with a large amount of material, we have found many substances in the sublimate and residue, the relation of which to the expected rearrangement products is shown in the diagram on next page.

When the gases from the decomposition were passed through water and through potassium hydroxide solution, the water was found to contain carbon dioxide, evidently from the interaction of cyanic acid and water vapor at the elevated temperature, and the alkaline solution was found to contain prussic acid and cyanic acid, substances which may very well have been produced as such by the decomposition or which may equally have been produced by the interaction of cyanogen, from the decomposition, with the alkali in the solution. The presence

<sup>6</sup> Franchimont and Umbgrove, *Rec. trav. chim.* 17, 287 (1898); Kranzler, *Bachelor's Thesis*, Mass. Inst. Tech. 1925.

<sup>7</sup> Werner, *Jour. Chem. Soc.* 123, 2577 (1923).

of cyanic acid in the products of decomposition was further substantiated by the isolation from the solid residue of its trimer, cyanuric acid, and from the sublimate of urea, formed evidently by the combination of cyanic acid and ammonia in the gas phase. Cyanamide was found in the sublimate, and its trimer, melamine, in the sublimate and in the residue. Melam and melem, formed from melamine by the loss, from two molecules, of one molecule and of two molecules respectively of ammonia, were also found in the residue



along with ammeline and ammelide, reaction products of cyanic acid with cyanamide. Mellon, a yellow material which is produced by the heating of any of these last named substances, was also found in the residue. When mellon is heated further, it breaks down into nitrogen, prussic acid, and cyanogen. Cyanogen polymerizes to paracyanogen. Paracyanogen was isolated from the residue and identified.

The residue from the decomposition weighed about 25% as much as the original nitroguanidine and contained slightly more than 20% of its own weight of the unstable  $\beta$ -form.

#### REACTIONS OF NITROSOGUANIDINE IN AQUEOUS SOLUTION.

Nitrosoguanidine explodes when heated or when treated with strong sulfuric acid. When warmed in aqueous solution, it breaks down, as Pellizzari has shown,<sup>8</sup> into cyanamide, water, and nitrogen—a reaction which appears to be plausibly explained by supposing that it dearranges into cyanamide and nitrosoamide and that the nitrosoamide on warming breaks down into nitrogen and water.



The hypothesis that the nitrogen comes from guanidine nitrite pro-

<sup>8</sup> Pellizzari, *Atti. accad. Lincei*. 31 [I], 171 (1921).

duced by the hydration of nitrosoguanidine, or from ammonium nitrite produced by the rearrangement of guanidine nitrite, is not tenable, for we have found that guanidine nitrite gives off no gas when boiled in aqueous solution.

The probable presence of nitrosoamide in an aqueous solution of nitrosoguanidine is further indicated by the fact that the solution yields nitrous acid under the hydrating action of hydrochloric acid. Nitrosoguanidine dissolves in cold conc. hydrochloric acid to form a yellow solution which gives off red oxides of nitrogen when it is warmed. Added to a cold acidified solution of dimethylaniline or of diphenylamine, nitrosoguanidine converts these substances into their nitroso derivatives.

#### EXPERIMENTS.

##### *Decomposition of Nitroguanidine by Hot Conc. Sulfuric Acid.*

The reaction was studied by heating a solution of 380 milligrams of nitroguanidine in 30 c.c. of conc. sulfuric acid in a 50 c.c. side-arm flask in an oil bath with a thermometer in the oil. The temperature was raised just rapidly enough to maintain an evolution of gas. The gas was collected over mercury in several portions which were analysed separately in order that it might be known which gases came off in greatest amount at the beginning. In an experiment in which the apparatus was filled with air at the start, gas evolution commenced at about 130° and five portions were collected below 223°, a total of 189.5 c.c. of gas, of which 28.0 c.c. was carbon dioxide, 74.5 c.c. nitrous oxide, 8.0 c.c. oxygen, and 78.1 c.c. nitrogen. Since 8.0 c.c. of oxygen is associated in the air with about 32 c.c. of nitrogen, it was apparent that considerable nitrogen had been produced from the nitroguanidine. Experiments were accordingly carried out in which the apparatus was filled with oxygen at the start and swept out with oxygen at the end. The results of a typical experiment, tabulated below, show that nitrous oxide comes off more rapidly than carbon dioxide and that considerable nitrogen is also produced.

	Temperature Interval	Volume of Sample (c.c.)	Composition of Sample (c.c.)			
			CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub> O	N <sub>2</sub>
First Sample	135°-170°	50.0	3.5	17.5	16.0	13.0
Second "	170°-220°	48.0	13.0	2.0	28.0	5.0
Third "	220°-270°	49.0	22.0	2.0	20.5	4.5
Fourth "	270°-315°	29.0	14.0	1.5	9.5	4.0
Fifth "	315°-330°	55.5	26.5	21.5	3.0	4.5
Total	135°-330°	231.5	79.0	44.5	77.0	31.0

*Nitrations with Nitroguanidine.*

Nine and four-tenths grams of aniline was dissolved in 25 c.c. of conc. sulfuric acid, the mixture being warmed until solution was complete, and finally cooled in ice. Ten and four-tenths grams of nitroguanidine was dissolved in 50 c.c. of conc. sulfuric acid at a temperature below 2°, and the solution was added, slowly and with stirring, to the aniline solution while the temperature was kept below 2°. After standing 24 hours, first in ice-water and later at room temperature, the mixture was poured into ice-water, made ammoniacal, and the precipitate was steam-distilled in vacuum. The distillate by extraction with ether yielded 1.9 grams (13.8%) of a mixture of *o*- and *m*-nitroaniline, solidification point 90°, and the residue, recrystallized from water, yielded 2.76 grams (19.7%) of *p*-nitroaniline, m.p. 147°.

In a similar experiment the temperature was kept below -4° during the mixing, and the crude nitro compounds were extracted with chloroform from the ammoniacal ice-water in which the mixture had been drowned. The chloroform deposited 13.4 grams of material 96% of the theoretical amount. Examined by the method described by Holleman and his co-workers,<sup>9</sup> this was found to consist of 6.5% *p*-nitroaniline, 46.7% *m*-nitroaniline, and 46.8% *o*-nitroaniline.

Phenol was nitrated by adding nitroguanidine to a solution of the substance in conc. sulfuric acid. After standing at room temperature, the mixture was heated for 10 minutes in the boiling water bath, diluted, and distilled with steam. The first portions of the distillate yielded about 20% of the theoretical amount of *o*-nitrophenol, and the later portions a small amount of 2, 4-dinitrophenol.

Three grams of acet-*p*-toluide was dissolved in 10 c.c. of conc. sulfuric acid and nitrated by the addition of 2.1 grams of nitroguanidine. After everything had gone into solution, the mixture was heated for 10 minutes in boiling water, diluted, chilled, filtered, and the product, recrystallized from water, yielded 1.94 grams of *m*-nitro-acet-*p*-toluide, orange-brown crystals, m.p. 96°.

Three grams of aniline in 8 c.c. of conc. sulfuric acid was nitrated with 1 gram of nitroguanidine in 5 c.c. of acid, and the mixture was poured into water, made ammoniacal, filtered, and treated with an excess of ammonium picrate solution. The precipitate, purified by washing with cold alcohol, hot water, and boiling ethyl acetate, yielded 0.402 grams of guanidine picrate, m.p. 311° with preliminary charring, 16% of the theory.

<sup>9</sup> Holleman, Hartogs, and Vanderlinden, *Ber.* 44, 1190 (1911).

*Reaction between Cyanamide and Ammonia in Aqueous Solution.*

One gram of lime-nitrogen, 5 grams of ammonium carbonate, and 50 c.c. of water were boiled together for 5 minutes. Ammonia came off in abundance, and the solution after filtration gave with ammonium picrate no precipitate whatever. The same amounts of the same materials, heated in a sealed tube for 2 hours at  $110^{\circ}$ , yielded a solution from which guanidine picrate corresponding to 0.0528 grams of guanidine was obtained.

If a substance like picric acid is present with which guanidine forms a sparingly soluble compound, then the combination of cyanamide with ammonia appears to take place fairly rapidly in ammoniacal solution. Twenty grams of lime-nitrogen was mixed with 50 c.c. of water, and 500 c.c. of water in which 25 c.c. of conc. sulfuric acid had been previously dissolved was added. The solution was filtered, made ammoniacal, again filtered, and allowed to stand over night with the addition of 80 c.c. of saturated ammonium picrate solution. The precipitate, collected the next morning and recrystallized from alcohol, yielded 0.406 grams of guanidine picrate, corresponding to 0.137 grams of guanidine.

*Reaction of Nitroguanidine with Ammonia.*

One gram of nitroguanidine in a glass capsule was treated with 15 c.c. of strong ammonia water (sp. gr. 0.90), and the mixture was evaporated to dryness on the steam bath. The residue had the appearance of nitroguanidine. After 10 such evaporations with ammonia water, a residue resulted which contained no needle crystals and gave no blue color with a solution of diphenylamine in conc. sulfuric acid. It effervesced with hydrochloric acid, and gave with ammonium picrate a precipitate of guanidine picrate of characteristic properties and melting point. In a similar experiment where the evaporation with ammonia was carried out 15 times, precipitation with ammonium picrate yielded 1.366 grams or 54.6% of the theoretical amount of guanidine picrate. In another where 16 evaporations were made, more rapidly than before, the yield of guanidine picrate amounted to 1.098 grams or 44% of the theory.

Fifteen grams of nitroguanidine and 400 c.c. of strong ammonia were introduced into a tall beaker and the solution was evaporated to dryness slowly on the steam bath during 13 hours. The almost colorless residue smelled of ammonia and, after drying, weighed 8 grams. After extraction with hot alcohol it left 5.2 grams, 40.3% of the theory,

of guanidine carbonate, identified by the picrate, by its effervescence with hydrochloric acid, and by melting point,  $205^{\circ}$ – $207^{\circ}$ , after solution in water and precipitation by the addition of alcohol. The alcohol extract of the residue was found to contain a further amount of guanidine carbonate along with urea, m.p.  $132^{\circ}$  after recrystallization from acetone, identified by mixed melting point with a known sample, by the biuret test, by its nitrate, m.p.  $150^{\circ}$ – $151^{\circ}$  (reported  $152^{\circ}$ ), and by its xanthidrol derivative, m.p.  $259^{\circ}$ – $260^{\circ}$  (reported  $260^{\circ}$ – $261^{\circ}$ ). Another experiment with the same amounts of nitroguanidine and of strong ammonia water, in which the evaporation was completed in 8 hours, yielded 7.3 grams of residue from which 5.14 grams of guanidine carbonate, 40.3% of the theory, was obtained. Another in which the evaporation was completed in 6 hours, yielded 7.72 grams of residue, from which 5.30 grams of guanidine carbonate, 41.2%, was obtained.

*Preparation of Guanidine Carbonate.* Two hundred and eight grams of nitroguanidine (2 mols), 300 grams of ammonium carbonate, and 1 liter of water were heated in the water bath, in a flask equipped with a reflux condenser and a thermometer dipping into the mixture, until the thermometer indicated  $65^{\circ}$ . Vigorous evolution of gas took place, and it was necessary to shake the flask from time to time to prevent the nitroguanidine from being carried up into the neck. After 10 hours at  $65^{\circ}$ , everything had gone into solution and the liquid did not deposit crystals on cooling. It was then heated with the flame and refluxed gently for 2 hours to complete the reaction. Ammonia came off in abundance and ammonium carbonate collected in the condenser. Evaporated to dryness on the steam bath, the liquid yielded 172.1 grams of dry crystalline material which was free from ammonium carbonate. This was stirred up with 200 c.c. of cold alcohol, filtered, and rinsed on the filter with more alcohol. The alcohol washings, evaporated on the water bath, yielded 2.4 grams of a mixture of urea and guanidine carbonate from which, by 3 recrystallizations from butyl alcohol, 0.7 grams of urea, 0.58%, was obtained. The residue from the alcohol washing was treated on the filter with just enough water to remove all soluble material, and left 4.5 grams of gritty insoluble matter which, recrystallized once from hot water, yielded 3.5 grams, 4.2%, of melamine. The water solution, diluted with 3 volumes of alcohol, gave a heavy, white, crystalline precipitate of guanidine carbonate. This was filtered off, and dried, and the liquors, evaporated on the steam bath, taken up in water, filtered, and precipitated with alcohol, yielded more of the same material. Total yield of guanidine carbonate, 162 grams, 90% of the theoretical amount.

Guanidine carbonate appeared to dearrange in warm aqueous solution, for a clear solution of the pure material when evaporated on the steam bath gave off ammonia and left a residue of impure guanidine carbonate which contained a few percent of melamine insoluble in water.

*Reaction of Nitroguanidine with Amines.*

Five grams of nitroguanidine and 15 c.c. of a 33% aqueous solution of methylamine were heated together in a sealed tube in boiling water for 1 hour. The product, treated with ammonium picrate and evaporated to dryness, yielded a residue from which methylguanidine picrate was extracted with alcohol. By recrystallization from alcohol in which it was very soluble, impure methylguanidine picrate, m.p. 193° (reported 200°–201.5°), was obtained, 1.01 grams, 7.3% of the theoretical amount. A few milligrams of material which appeared to be melamine was also present and a mixture of picrates, m.p. 137°–145°, from which nothing definite could be isolated.

In experiments with dimethylamine, no evidence was obtained of dimethylguanidine either as the picrate or as dimethylguanidine platinum chloride which is reported to have a characteristic appearance under the microscope.

Nine and four-tenths grams of aniline, 10.4 grams of nitroguanidine and 125 c.c. of water were boiled together under reflux for 50 hours. The suspended matter, filtered from the hot liquid and recrystallized from alcohol, yielded 2.570 grams of *sym*-diphenylurea, 23% of the theoretical amount. The aqueous filtrate, steam distilled for the removal of aniline and concentrated to a small volume, yielded a few crystals of phenylurea, and, on the addition of ammonium picrate, a very small amount of phenylguanidine picrate which was recrystallized from alcohol and showed a meniscus at 210°, melting completely at 214°.

When 10.4 grams of nitroguanidine and 50 c.c. of aniline were refluxed together in the absence of water for 16 hours, none of these products were obtained. Seven and thirty one-hundredths grams of nitroguanidine was recovered from the mixture and 2.50 grams of other material which appeared to be a mixture of phenylated melamines, for it yielded three fractions one of which did not melt at 300° while the others melted respectively at 189° and at 219°. It was not examined further. No evidence of phenylguanidine was found.

*Methylnitroguanidine.* A mixture of 15 grams of nitroguanidine

and 55 c.c. of an aqueous 28% solution of methylamine was warmed in a flask under reflux on the steam bath. The mixture effervesced with the evolution of ammonia, and at the end of about 10 minutes, during which time the temperature had risen to about 70°, all of the nitroguanidine had gone into solution. The solution, chilled and filtered, yielded a crystalline mass which was found to consist of a mixture of nitroguanidine with methylnitroguanidine. By extraction with absolute alcohol and recrystallization of the extract, 6.08 grams of methylnitroguanidine was obtained, 35.8% of the theoretical amount. The aqueous filtrate from the chilled reaction mixture was concentrated by slow evaporation for several days; finally carbon dioxide was bubbled through—and crystals of carbonate, m.p. 153°–154°, separated. These effervesced with hydrochloric acid, and, on treatment with ammonium picrate, yielded methylguanidine picrate, m.p. 199.8° (reported 200°–201.5°).

Methylnitroguanidine was obtained in better yield, about 45%, by warming nitroguanidine with an aqueous solution of one equivalent of methylamine (thermometer in the mixture) in the water bath at 65°–70°. When all of the nitroguanidine had gone into solution at this temperature (after about 35 minutes), the solution was chilled, filtered, and worked up with alcohol. Alpha- and beta-nitroguanidine were found to yield identical methylnitroguanidine.

Methylnitroguanidine crystallizes from alcohol in colorless, short, glistening prisms, m.p. 160.5°–161.0°. Molecular weight by the boiling point method in alcohol solution: found 122.5, 121; calculated 118. Nitrogen by combustion: found 46.95%, 47.04%; calculated total nitrogen 47.45%. Nitrogen by nitrometer: found 11.81%, 11.78%; calculated nitro group nitrogen 11.86%.

Methylnitroguanidine dissolved readily in conc. sulfuric acid to yield a colorless solution. When such a solution was warmed, a gas which inflamed a glowing splint began to come off abundantly at 70°, the later portions of gas did not inflame a glowing splint, and gas evolution was complete when 240° had been reached. The acid liquid after cooling was diluted with water, made alkaline with sodium hydroxide, and distilled. Methylamine was identified in the distillate by its picrate, m.p. 205° (reported 207°) and by its chloroplatinate, m.p. 224° (reported 224°). The production of methylamine when methylnitroguanidine is decomposed by hot conc. sulfuric acid is taken as proof that the methyl group, as would be expected, is not attached to the same nitrogen atom as the nitro group.

Although nitroguanidine and methylamine react rapidly in aqueous

solution at 65°–70° to produce methylnitroguanidine, the results are entirely different if the solution is evaporated to dryness on the steam bath. In several experiments, the residues from the evaporation were gummy materials refractory to all attempts at crystallization. On solution in water or alcohol and precipitation with ammonium picrate they yielded a picrate which melted, after several recrystallizations from alcohol, at 160°.

*Benzylnitroguanidine.* Twelve and one-half grams of benzylamine was diluted with 50 c.c. of water, 12 grams of nitroguanidine was added, and the mixture was warmed at 65° for 40 minutes. The nitroguanidine disappeared, but crystals of a new kind appeared as a froth on the surface of the liquid. The mixture was chilled and filtered, and the solid material, recrystallized from alcohol, yielded 9.16 grams, 40.9%, of benzylnitroguanidine. The aqueous filtrate on evaporation yielded a sticky mass from which a few crystals separated. These, recrystallized from alcohol, melted at 147° and were identified as benzylurea by mixed melting point with a known sample.

Benzylnitroguanidine crystallizes from alcohol, in which it is not very soluble, in colorless needles, m.p. 183.5°. Molecular weight by the boiling point method in alcohol solution: found 193,196; calculated 194. Nitrogen by combustion: found 28.73%, 28.61%; calculated 28.86%. Benzylnitroguanidine chars and heats up when treated with conc. sulfuric acid, and the warm mixture evolves sulfur dioxide. It is less soluble in water than nitroguanidine itself, and requires about 1050 parts of cold water and 200 parts of boiling water for solution.

Other alkyl nitroguanidines were prepared by the method which had been found to work best for the preparation of methylnitroguanidine, and were obtained in yields equal to about 45% of the theoretical amount.

*Ethylnitroguanidine*, from ethylamine and nitroguanidine, colorless cubes from alcohol, m.p. 147°–148°. Nitrogen by combustion: found 42.01%, 42.33%; calculated total nitrogen 42.42%. Nitrogen by nitrometer: found 10.58%, 10.54%; calculated nitro group nitrogen 10.61%.

*n-Butylnitroguanidine*, from *n*-butylamine and nitroguanidine, crystallizes from alcohol, in which it is readily soluble, in long prisms. It melts under water at about 65°. If taken up in water at 60°, it is deposited from the cold solution in colorless stout needles, m.p. 84°–85°. Nitrogen by combustion: found 34.84%, 34.90%; calculated total nitrogen 35.00%. Nitrogen by nitrometer: found 8.73%, 8.72%; calculated nitro group nitrogen 8.75%.

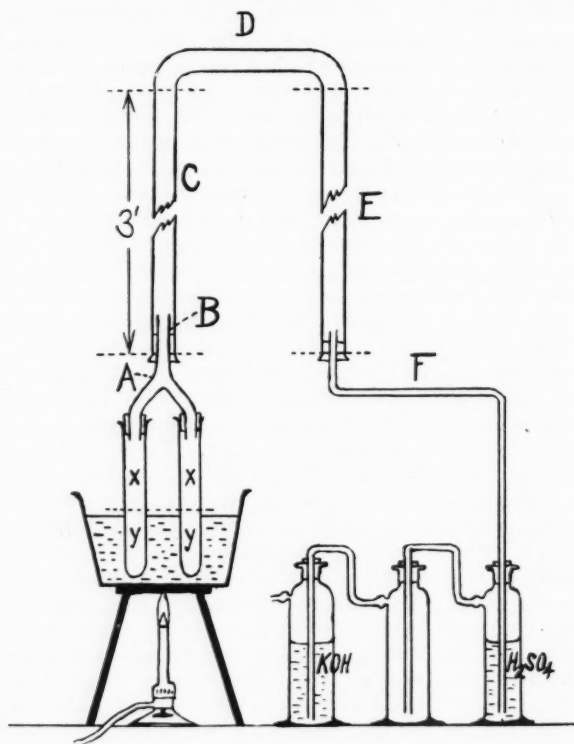
*Decomposition of Nitroguanidine by Heat.*

A wide-mouth flask was heated in the oil bath at 235°–250°, and 30 grams of nitroguanidine was introduced in small portions at a time, each portion being allowed to decompose before the next portion was added. Fumes containing water and ammonia came off, a sublimate condensed in the upper part of the flask, and a buff-colored residue collected, practically all in one place, on the bottom. About an hour was required for the addition of all of the nitroguanidine, and, in consequence, the first portions of the residue were subjected to the action of the high temperature throughout this period. The residue weighed 7.90 grams, 26.3% of the weight of the original nitroguanidine, and was more deeply buff-colored than the residue of another experiment in which the heating was not continued so long. By extraction with boiling water, cyanuric acid and melamine were obtained from it. The former was identified by the fact that it sublimed without melting and by the preparation of its copper-ammonia complex salt of lilac color and characteristic appearance under the microscope. The latter was sparingly soluble in cold and readily soluble in hot water, from which it crystallized in characteristic rhomb-shaped plates. Its aqueous solution gave a blue-green precipitate with 1% copper sulfate solution, and with 0.1 N silver nitrate a white crystalline precipitate, soluble in ammonia, soluble in considerable boiling water, and soluble in strong silver nitrate solution by heating. The solution in strong silver nitrate deposited on cooling a white crystalline precipitate which, after separation from the liquors, was converted into an amorphous powder by the addition of strong ammonia water and dissolved in a further quantity of the same reagent. The sublimate in the upper part of the flask was found to consist of two kinds of crystals, needles and plates. A portion of each kind was separated by hand-picking; the plates were identified as melamine, while the needles melted at 131° and were identified as urea by mixed melting point with a known sample, m.p. 132°. No urea was found in another experiment where the residue had not been heated for any considerable time after the first decomposition was complete.

In another experiment the nitroguanidine was decomposed in the apparatus represented in the figure.

The nitroguanidine, already crystallized 3 times, was crystallized a fourth time by the rapid cooling of its solution in hot water, and the fluffy mass of fine crystals which resulted was decomposed in 8" test tubes heated in the oil bath. The vapors passed through the long wide condenser in which the solid material was deposited, and the re-

maining gases passed into wash bottles. The letters and dotted lines of the figure indicate the pieces into which the apparatus was cut after the experiment, thus making possible the separate examination of the residue and of the various portions of the sublimate. Between half a gram and a gram of material was introduced into a test tube



which was connected to the apparatus and heated until decomposition was over. The tube was then removed and another containing fresh nitroguanidine was put in its place. More nitroguanidine was introduced, on top of the residue from the decomposition, into the tube which had been removed, and the tube was again connected with the apparatus and heated in place of some other tube which had been

removed. In each run 6 tubes were used in rotation, and each of these at the end of the run contained the decomposition products from about 20 grams of nitroguanidine. The sublimate condensed almost entirely in the wide tubes; only a very thin film of material was found in the tube, F. A total of 574.5 grams of nitroguanidine was decomposed in 5 runs, as follows:

Weight of Nitroguanidine.	Temperature of Oil Bath.	Weight of Residue.	Residue as percent of Nitroguanidine.
104.5 grams.	233°-235°	27.0 grams.	25.7%
112.0 "	234°	28.7 "	25.6%
104.0 "	234°-235°	24.2 "	23.1%
124.2 "	234°	29.6 "	23.8%
129.8 "	233°-237°	33.0 "	25.4%
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574.5 "		142.5 "	24.8%

*Gaseous Products.* In the first run the gases were passed into water, and the water was found to contain carbon dioxide but neither prussic acid nor cyanic acid. The potassium hydroxide solution which was used in the later runs was found to contain prussic acid by the Prussian blue test, and cyanic acid by Werner's test with copper sulfate, pyridine, and chloroform. The water which was produced during the decomposition condensed in large part in the vertical tube and was found at the end of the experiment in the trap formed by the upper end of the branched tube, A.

*The Sublimate.* The branched tube, A, contained about 13 grams of solid material from which 8.5 grams of  $\beta$ -nitroguanidine was isolated. This was identified by qualitative tests for nitroguanidine, by conversion into  $\alpha$ -nitroguanidine under the influence of strong sulfuric acid, and by measurement of the indices of refraction which were found to be identical with those which have been reported elsewhere. The remainder of the material consisted of melamine along with a small quantity of insoluble amorphous matter which was not examined further. Similar amorphous matter was found in the other portions of the sublimate.

The lower part, B, of the vertical tube afforded only a very small amount of pasty material. When this was extracted with cold water, the extract gave with copper sulfate a black precipitate of copper cyanamide and with ammoniacal silver nitrate a yellow precipitate of silver cyanamide. When a portion of the pasty mass was dried in the oven, it turned slightly yellow, gave off the odors of ammonia and

prussic acid, and yielded a meager residue from which melamine was isolated.

The material in the upper part, C, of the vertical tube gave a distinct test for cyanamide, but was found to consist largely of  $\beta$ -nitroguanidine and melamine, along with a small amount of insoluble amorphous material.

Very little material was deposited in the rest of the condensing train, in the tube, D, only enough material barely to cover its walls. The deposit gave a distinct test for cyanamide and a faint test for nitroguanidine, and was found to consist almost entirely of melamine along with a small amount of amorphous material. The small amounts of material in E and in F were found to be of the same nature except that they appeared to be entirely free from nitroguanidine.

The material scraped out of the upper portions of the 8" test tubes, after these had been cut in two, weighed 15.5 grams and consisted of cyanamide, melamine, both  $\alpha$ - and  $\beta$ -nitroguanidine, and a small amount of insoluble amorphous material.

From the entire sublimate 5.5 grams of melamine and 13.0 grams of  $\beta$ -nitroguanidine were isolated.

*The Residue.* After a preliminary examination of portions of the residue, a method for the separation of the various substances was worked out on the basis of their previously known properties, and the composition of an average sample of the residue was determined with satisfactory accuracy.

A 69 grams sample after an hour of refluxing with 700 c.c. of methyl alcohol left 52.8 grams of material undissolved and yielded a solution from which 10.8 grams of practically pure  $\beta$ -nitroguanidine was obtained on evaporation. The residue from the alcohol extraction was extracted with 3 liters of hot water, and the extract on evaporation yielded 7.0 grams of a mixture of melamine and  $\beta$ -nitroguanidine. The  $\beta$ -nitroguanidine was converted into readily soluble methyl-nitroguanidine by digesting the mixture on the steam bath for a few minutes with aqueous methylamine solution. The melamine, which was not affected, was filtered from the cold solution, and dried—and weighed 3.22 grams. The residue which remained after the first hot water extraction was again extracted with 3 liters of boiling water. The filtrate on cooling deposited 1.300 grams of ammeline, and on evaporation yielded further 0.950 grams of material which gave only a very faint test for nitroguanidine.

The original residue from the decomposition of nitroguanidine was

slightly buff-colored. The extractions with alcohol and with water had removed colorless substances, and the material which now remained (49 grams) was intensely yellow colored. The presence of mellon in this material was thought to be sufficiently demonstrated by the color, for mellon is the only substance of this series which is colored, and by the fact that the color was discharged by potassium hydroxide solution in accordance with the known behavior of mellon. The residue was now extracted with 2 liters of hot dilute (about 7%) sodium carbonate solution, and the washings, on chilling deposited 7.5 grams of ammeline and, on neutralization with acetic acid, 0.100 gram of ammelide.

The 41 grams of yellow material which remained was treated successively with 2 portions of 650 c.c. of 10% aqueous potassium hydroxide solution, warmed to 90°, and filtered quickly with suction. The filtrates on cooling deposited 4.7 grams of melam, and, on acidification with acetic acid, 28.7 grams of ammelide.

The residue which now remained was of a grayish color. When warmed to boiling with 60 c.c. of 33% aqueous potassium hydroxide solution, it yielded a deep brown colored solution from which only 0.06 gram of undissolved material was removed by filtration. The strongly alkaline filtrate gave an abundant precipitate on cooling. It was acidified completely and yielded 3.600 grams of melam and melem.

The brownish-black bulky material which survived the treatment with strong alkali was identified as paracyanogen. It dissolved to form a brown solution in hot strong alkali and in hot strong sulfuric acid. It was precipitated again by dilution of the sulfuric acid solution. When a small quantity was heated in a hard glass tube, a white sublimate formed at first and disappeared on further heating, a brown sublimate was formed farther up in the tube, the glass was attacked and became grayish, opaque, and filled with little bubbles—and the gas which escaped smelled like cyanogen and burned with a purplish flame. When the gas was passed first into silver nitrate solution and then into potassium hydroxide solution, a white precipitate was produced in the silver nitrate, which showed that the paracyanogen was not entirely pure, and the potassium hydroxide solution was found to contain prussic acid and cyanic acid.

The analysis of the 69 gram average sample of the residue from the decomposition of nitroguanidine is summarized, as follows:

$\beta$ -Nitroguanidine.....	14.6 grams.	21.2%
Melamine.....	3.2 "	4.6%
Ammeline.....	8.8 "	12.8%
Ammelide.....	28.8 "	41.7%
Melam.....	4.7 "	6.6%
Melam and Melem.....	3.6 "	5.2%
Paracyanogen.....	0.06 "	0.1%
Mellon and unaccounted for.....	5.2 "	7.5%

*Nitrosations with Nitrosoguanidine.*

Two and seven-tenths grams of dimethylaniline was dissolved in a mixture of 20 c.c. of water and 7 c.c. of conc. hydrochloric acid. Two grams of nitrosoguanidine was added and went rapidly into solution forming an orange-red liquid. After 10 minutes crystals began to separate. After half an hour the mixture was chilled and the orange colored crystals were filtered off and rinsed with a little water. Dissolved in water, made alkaline, and extracted with ether, they yielded 1.0 gram of crude product which on recrystallization from benzene with the addition of petroleum ether, gave 0.8 gram of pure *p*-nitrosodimethylaniline, m.p. 85.5°, grass-green leaflets, identified by mixed melting point with a known sample.

Two grams of diphenylamine was dissolved in 20 c.c. of alcohol, 2 grams of nitrosoguanidine and 5 c.c. of conc. hydrochloric acid were added, and the mixture was allowed to stand for three-quarters of an hour. The mixture was then diluted with water, and the precipitate, collected, dried, and recrystallized from ligroin, yielded 0.84 gram of pure diphenylnitrosamine, m.p. 65.5°, identified by mixed melting point with a known sample.

SUMMARY.

A solution of nitroguanidine in strong sulfuric acid apparently contains two substances, one of which gives off nitrous oxide readily on warming, while the other gives off carbon dioxide more slowly on stronger heating. The production of nitrous oxide is not quantitative, but the gases contain elementary nitrogen—as would be expected if nitroamide were present in the solution.

A solution of nitroguanidine in strong sulfuric acid is a suitable reagent for the nitration of certain aromatic substances. After the nitric acid has been removed from such a solution, cyanamide appears to be left.

Similarly, nitrosoguanidine in the presence of hydrochloric acid converts certain aromatic substances into their nitroso derivatives.

The reactions of nitroguanidine in aqueous solution support the belief that it dearranges in this solvent to produce, on the one hand nitroamide and cyanamide, on the other hand nitrocyanamide and ammonia. Thus, it reacts, on the one hand, with ammonia to give guanidine, with ammonium carbonate to give guanidine carbonate in excellent yields, with methylamine to give methylguanidine, and, on the other hand, with ammonia to give urea, with aniline to give phenylurea, with methylamine etc. to give methylnitroguanidine etc., and with benzylamine to give benzylurea and benzylnitroguanidine. Methyl-, ethyl-, *n*-butyl-, and benzyl-nitroguanidine are described.

When  $\alpha$ -nitroguanidine is heated to decomposition, it is converted in part into  $\beta$ -nitroguanidine and in part decomposes to yield the products which would be expected from the dearrangement. Water, ammonia, cyanamide, cyanuric acid, urea, melamine, ammeline, ammelide, melam, melem, mellon, and paracyanogen have been found among the products.

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